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THE SORPTION OF SOAP BY TEXTILE FIBERS[1]

A. S. WEATHERBURN,[2] G. R. F. ROSE,[2] AND C. H. BAYLEY[2]

Abstract

The sorption of the sodium soaps of lauric, myristic, palmitic, stearic, and oleic acids from aqueous solutions by various textile fibers has been measured. The sorption of both the fatty acid and alkali components of the soaps by dull acetate rayon and dull nylon fibers was essentially the same as that shown by the corresponding bright (undelustered) fibers, while dull viscose rayon sorbed considerably more fatty acid than the bright fiber. In general, the order of increasing sorption was: cotton, nylon, acetate, bright viscose, dull viscose, and wool. Of the saturated soaps, the maximum sorption of fatty acid by all fibers was obtained with sodium myristate, while the alkali sorptions were approximately the same for myristate, palmitate, and stearate, all of which were higher than for laurate. The sorption from sodium oleate solutions corresponded approximately to that from the C_{14}–C_{16} saturated soaps. Preferential sorption of alkali by cotton and viscose rayon was observed for all soaps, while acetate rayon, nylon, and wool showed preferential sorption of fatty acid with the lower molecular weight soaps and preferential sorption of alkali with the higher soaps. Suppression of hydrolysis by the addition of excess free alkali resulted in a reduction in fatty acid sorption in every case, and shifted the maximum from the C_{14} to the C_{16} soap. It is concluded that the sorption of soap by textile fibers is a complex process involving the more or less independent sorption of neutral soap, hydrolytic fatty acid (or acid soap), and hydrolytic alkali.

Introduction

During the course of studies in the field of detergency currently in progress in these laboratories, it became of interest to obtain comparative data relating to the sorption of various soaps by textile fibers.

Some work dealing with the sorption of soaps by textile fibers has been reported (1, 2, 4, 6, 8, 18, 28), but for the most part the experimental conditions and methods employed have been too varied to permit a comprehensive comparison of data for the various soaps and fibers. Such factors as initial concentration of soap, temperature, duration of contact of fiber with solution, degree of agitation, and ratio of fiber to solution may be expected to influence the amount of sorption obtained, and there has been little uniformity with respect to these factors in the work so far reported. Some of the published methods (1, 2, 6, 8) do not distinguish between the sorption of the fatty acid and alkali components of the soap, and since in general there is selective

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[2]*Chemist.*

sorption of one or other of these components, data based on such methods may be considered inadequate.

A number of other investigators have studied the sorption of surface-active materials by textile fibers, but their work has been confined primarily to the newer synthetic compounds (3, 13, 19, 20, 22). A review of the literature and comparison of available data is given by Harris (9).

The present paper gives data relating to the sorption of the fatty acid and alkali components of a number of pure soaps by a range of textile fibers. The experimental conditions and analytical techniques were carefully standardized and maintained constant throughout, so that direct comparisons of data for the various soaps and fibers are possible.

Experimental

Materials and Methods

Soaps

Sodium soaps of lauric, myristic, palmitic, and stearic acids were prepared as described previously (27). Sodium oleate was made directly as a 1% aqueous solution by heating a weighed quantity of oleic acid of the grade previously used (27) with the equivalent amount of carbonate-free sodium hydroxide solution and diluting with water to exactly 1% concentration. This stock solution was further diluted as required for use.

Distilled water, freshly boiled-out and cooled in the absence of carbon dioxide, was used in the preparation of all solutions.

Cotton

Fully bleached cotton fabric (a nainsook manufactured under the name of Tarantulle, by Messrs. Tootal and Broadhurst Lee Co., Manchester, England) having a thread count of approximately 100 × 100 threads per inch and a weight of 2.7 oz. per sq. yd., was extracted for 24 hr. in a Soxhlet apparatus with 1 : 1 (by volume) methanol–benzene. After air-drying to eliminate solvent, the fabric was immersed for 18 hr. in $N/100$ hydrochloric acid and then rinsed in distilled water until the rinsings were neutral to methyl orange. The fabric was finally immersed for one-half hour in boiling water and rinsed four times in cold water.

Viscose Rayon

Bright yarn, 150 denier, 36 filament, and dull yarn, 150 denier, 40 filament, were used. These yarns were stated by the manufacturer to contain practically no finishing material. The preliminary treatment was the same as for cotton except that the final boiling in water was omitted. The ash content of the dull yarn was 1.6% and consisted essentially of titanium dioxide.

Acetate Rayon

Bright and dull acetate rayon yarns were used. These yarns were both 150 denier, 40 filament, 3½ Z twist, prepared without the use of any lubricant.

The acetic acid yield of the bright yarn was 54.3% and of the dull yarn 52.7% as determined by the method of Howlett and Martin (10). The ash content of the dull yarn was 1.3%, consisting essentially of titanium dioxide. The preliminary treatment consisted of extraction for 24 hr. in a Soxhlet apparatus with benzene, followed by a thorough rinsing with distilled water.

Nylon

Bright and dull nylon yarns, both 70 denier, 34 filament, 1 Z twist were used. The yarns as received contained approximately 0.25% of finishing oils, but this material was removed in the preliminary treatment, which was the same as for acetate rayon. The ash content of the dull yarn was 0.3%.

Wool

Canadian fleece wool of 46^s quality, unscoured, obtained from Messrs. Ayers Co., Lachute, Quebec, was used. The wool was given a preliminary picking over to remove extraneous matter, and, as far as possible, the tips were removed. The material was extracted for 24 hr. in a Soxhlet apparatus with benzene, air-dried, and rinsed in four to five changes of distilled water. The wool was then picked over again to remove all visible extraneous matter and thoroughly rinsed with water until the rinsings were perfectly clear and colorless. (Approximately 15 changes of water were used.)

All fibers were conditioned at 70 ± 2° F. and 65 ± 2% R.H. for at least 24 hr. prior to use.

Procedure

A 6.000 gm. portion of the conditioned fiber was placed in a previously warmed 200 ml. vacuum bottle and agitated for 30 min.* with 150 ml. of 0.1% soap solution at 70° C., using a mechanical shaking device. After shaking, the equilibrium solution was immediately poured off and a 100 ml. aliquot was taken for analysis. A similar analysis was also carried out on a 100 ml. aliquot of the original soap solution. The fatty acid and alkali content of these solutions was determined as described previously (27). During the ether extraction of fatty acid from those solutions which had been in contact with wool or nylon fibers, some difficulty was encountered owing to the formation of emulsions, but this was overcome by the addition of 50 ml. of isopropyl alcohol prior to the first extraction. Analysis of the original soap solution with and without the use of isopropyl alcohol indicated that this reagent had no effect on the determination.

The sorption of either fatty acid or alkali is given by the formula

$$X = 0.025\ F\ (C_o - C),$$

where X = sorption, millimoles per gm. dry fiber,
C_o = concentration of reference solution, millimoles per liter,
C = concentration of equilibrium solution, millimoles per liter,
F = correction factor for moisture content of the conditioned fiber (See Table I).

**See "Rate of Sorption" below.*

Moisture Content of Conditioned Fibers

The moisture content of the conditioned fibers was determined by drying weighed samples to constant weight at 105° C. and reweighing. (See Table I)

Water of Hydration

The apparent sorption of soap as determined by the titration difference method given above is subject to error depending on the extent to which water is preferentially sorbed from the soap solution by the fiber, i.e., water taken up in this manner is no longer available for dilution of the soap and results in low values for the sorption data. The appropriate correction is given by Sookne and Harris (24) as follows:

$$A = C\,(B - \mathrm{W}),$$

where A = correction to be added to apparent sorption data,
C = equilibrium concentration, molar,
B = weight, in grams, of water selectively sorbed per gram of dry fiber,
W = original moisture content of fiber, grams water per gram dry fiber.

The "water of hydration" of the various fibers (i.e., water preferentially sorbed by, or entering into chemical combination with, the fiber) was determined by a modification of Champetier's method (5). A weighed sample of fiber was agitated for 30 min. in a solution of sodium thiosulphate (125 gm. per liter) at 70°. The sample was removed, pressed between sheets of blotting paper, and transferred to a weighing bottle. After weighing, the amount of sodium thiosulphate contained in the sample was determined iodimetrically. The weights of sodium thiosulphate and of water (by difference) per 100 gm. dry fiber were then calculated. This procedure was repeated four times with fresh fiber samples, using varying degrees of pressure on the blotting paper. On plotting the percentage of sodium thiosulphate in the samples against the percentage of water a straight line was obtained, which, when produced, cut the water axis to the right of the origin. This procedure was repeated using a more concentrated solution of sodium thiosulphate (250 gm. per liter) and a second straight line was obtained which had a greater slope than the first, but which, when produced, cut the water axis at essentially the same point. This point was taken as representing the "water of hydration" of the fiber. The results are recorded in Table I. The method as here applied is perhaps open to some criticism in that a fiber may not preferentially sorb the same amount of water from a soap solution as from a solution of sodium thiosulphate. The data should, however, serve to indicate the order of magnitude of the correction factor.

On applying this correction to a 0.1% sodium laurate solution, the value of A for any of the fibers was not greater than 0.0001 millimole per gm. and for the higher molecular weight soaps it was still smaller. Since this is considerably less than the probable error involved in the sorption determinations, no correction was made for water of hydration.

TABLE I

MOISTURE CONTENT AND WATER OF HYDRATION OF FIBERS

Fiber	Moisture content of conditioned fiber, %	Correction factor, *F*	Water of hydration, % (based on dry weight of fiber)
Cotton	6.92	1.074	5.0
Viscose Bright	11.60	1.130	15.0
Viscose Dull	11.48	1.128	15.0
Acetate Bright	6.53	1.070	8.2
Acetate Dull	6.53	1.070	7.8
Nylon Bright	3.98	1.041	2.8
Nylon Dull	3.75	1.040	2.8
Wool	13.66	1.158	14.0

Rate of Sorption

The sorption of soap by each of the fibers from solutions of sodium myristate was determined, using shaking times of 30 min. and 120 min. It was found that for all practical purposes equilibrium was established within the first 30 min., the amount of additional sorption taking place in 120 min. being less than the probable error involved in the determination.

Temperature

The data reported in this paper were obtained at 70° C. A limited study of sorption at 30° and 50° C. was carried out with viscose, acetate, and cotton but there did not appear to be any significant differences in the values obtained at these three temperatures. In the case of wool, measurements at 30° and 70° C. appeared to indicate a small but significant increase at the higher temperature.

Sorption of Soaps

The sorption of fatty acid and of alkali from 0.1% solutions of the various soaps by each of the fibers was determined at 70° C. For the sake of comparison, the sorption of alkali from 0.015% solutions of sodium hydroxide at 70° C. was also determined. The molar concentration of these solutions corresponded approximately to the total alkali concentration of a 0.1% solution of sodium palmitate. In order to compensate for the variation encountered in analytical results, a comparatively large number of replicate determinations were carried out. The data are given in Table II and Fig. 1.

A series of similar measurements was made in which the initial solutions contained 0.1% of soap and 0.01% of added sodium hydroxide. These data, together with the corresponding data for the soaps without added alkali, are given in Table III.

Discussion

The data of Table II indicate that the sorption of fatty acid and of alkali by dull acetate and nylon fibers is not significantly different from that by the corresponding bright fibers. Consequently, in Fig. 1 no distinction is made

TABLE II

SORPTION OF FATTY ACID AND ALKALI COMPONENTS OF SOAPS

Fiber	Sorption, millimoles/gm. fiber × 10^4												
	Sodium laurate		Sodium myristate		Sodium palmitate		Sodium stearate		Sodium oleate		Sodium hydroxide		
	Fatty acid	Alkali	Fatty acid	Alkali	Fatty acid	Alkali	Fatty acid	Alkali	Fatty acid	Alkali			
Cotton	13 ±5 (6)*	19 ±3 (6)	42 ±4 (10)	44 ±1 (10)	30 ±2 (6)	52 ±2 (6)	28 ±6 (16)	51 ±5 (16)	36 ±4 (6)	56 ±6 (6)	53 ±4 (6)		
Viscose Bright	97 ±7 (6)	180 ±5 (6)	144 ±10 (17)	311 ±9 (17)	77 ±5 (6)	312 ±5 (6)	45 ±3 (12)	291 ±4 (12)	64 ±8 (6)	274 ±7 (6)	311 ±3 (6)		
Viscose Dull	171 ±11 (6)	194 ±5 (16)	335 ±26 (12)	340 ±23 (11)	164 ±7 (9)	342 ±3 (6)	57 ±6 (12)	302 ±8 (12)	139 ±14 (6)	293 ±6 (6)	301 ±7 (6)		
Acetate Bright	77 ±5 (8)	52 ±4 (9)	132 ±9 (21)	86 ±23 (21)	81 ±0.2 (6)	108 ±2 (6)	48 ±5 (12)	87 ±3 (12)	111 ±9 (16)	103 ±7 (6)	161 ±11 (6)		
Acetate Dull	90 ±11 (7)	54 ±4 (9)	152 ±13 (10)	108 ±7 (10)	88 ±3 (11)	110 ±5 (11)	50 ±4 (12)	94 ±4 (12)	119 ±7 (6)	105 ±7 (6)	153 ±12 (6)		
Nylon Bright	43 ±5 (10)	17 ±8 (10)	102 ±25 (15)	53 ±5 (15)	79 ±4 (11)	61 ±3 (11)	49 ±3 (18)	77 ±4 (18)	82 ±5 (6)	80 ±7 (6)	80 ±5 (6)		
Nylon Dull	42 ±9 (10)	16 ±4 (9)	118 ±12 (10)	75 ±7 (11)	93 ±4 (11)	78 ±6 (12)	44 ±8 (18)	83 ±6 (18)	80 ±7 (6)	74 ±1 (6)	108 ±7 (6)		
Wool	140 ±20 (16)	95 ±6 (16)	397 ±23 (18)	316 ±18 (18)	279 ±19 (12)	371 ±16 (12)	112 ±23 (6)	288 ±15 (6)	386 ±7 (6)	413 ±13 (6)	733 ±39 (6)		

**Figures in parentheses indicate the number of replicate determinations.*

between the bright and dull forms of these fibers, average values being used in each case. The data for dull viscose, however, are significantly higher than those for the bright fiber, particularly with respect to the sorption of fatty acid. This difference is apparently not due entirely to the presence of the delustering pigment (titanium dioxide) since the two forms of acetate fiber did not show a similar difference although the amount of pigment in the dull acetate (1.3%) was only slightly less than that in the dull viscose (1.6%).

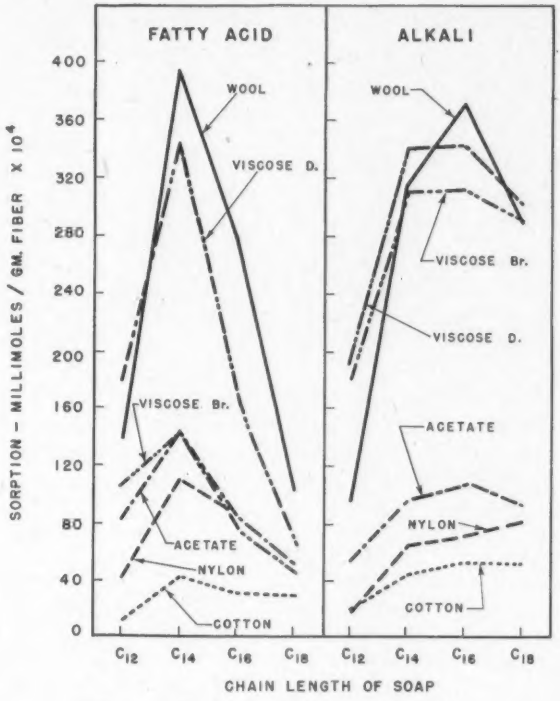

FIG. 1. *Sorption of soaps by various fibers.*

Of the saturated soaps studied, sodium myristate gave the highest sorption of fatty acid with all fibers, while on the basis of alkali sorption there was little difference between myristate, palmitate, and stearate, all of which showed considerably greater sorption than laurate. This is in general agreement with the findings of Colt and Snell (6) for cotton, if allowance is made for the fact that their data are expressed on a weight rather than a molar basis and do not distinguish between fatty acid and alkali sorption. There appears to be no obvious correlation between the sorption data for the various soaps and such properties as surface tension lowering (14, 26), solubility (17, 23), or degree of hydrolysis (15, 21), all of which might be expected to have some influence on the amount of sorption. Data for the critical micelle

concentration of the soaps, derived from various sources (7, 11, 12, 25), are summarized in Table IV. Some of the data are for potassium soaps, but values for the corresponding sodium soaps are said to be identical (11). In spite of considerable variation in the data obtained by different methods, it

TABLE III

EFFECT OF ADDED ALKALI ON SORPTION OF FATTY ACID FROM SOAP SOLUTIONS

Fiber	Sorption, millimoles/gm. fiber × 10^4							
	Sod. laurate		Sod. myristate		Sod. palmitate		Sod. stearate	
	*A**	*B*†	*A*	*B*	*A*	*B*	*A*	*B*
Cotton	13	0	42	11	30	21	28	10
Viscose, Br.	97	0	144	0	77	32	45	42
Viscose, Dull	171	—	335	35	164	91	57	—
Acetate, Br.	77	0	132	34	81	69	48	26
Nylon, Br.	43	0	102	7	79	18	49	16
Wool	140	0	397	277	279	183	112	64

**A—0.1% soap solution.*
†*B—0.1% soap + 0.01% sodium hydroxide.*

seems probable that the concentration of soap used in the present work (0.1%) lies below the critical micelle concentration for laurate and myristate, and above it for palmitate and stearate. The significance of this fact in relation to the sorption data is not clear, but it is probable that the fatty

TABLE IV

CRITICAL MICELLE CONCENTRATION OF SOAPS AT 50° TO 70° C.

Soap	Critical micelle concentration, %
Laurate	0.44 – 0.93
Myristate	0.18 – 0.25
Palmitate	< 0.028 – 0.089
Stearate	0.024

acid sorption is influenced by the state of aggregation of the soap at the particular temperature and concentration employed. It is of interest to note that the sorption of saturated soaps by carbon black increases in a more or less regular manner with increasing molecular weight of the soaps (27), and is of a higher order of magnitude than the sorption by fibers.

It has been shown previously (27) with respect to the sorption of soaps by carbon black that the presence of the double bond in sodium oleate results in a shortening of the effective chain length. This is confirmed by the present

data, since the sorption of fatty acid from sodium oleate solutions corresponds in general to that from the C_{14}–C_{16} saturated soaps, while the alkali sorption is of the same order as that of the C_{14}–C_{18} soaps.

Comparison of the various fibers shows that they may be arranged in order of increasing sorption of fatty acid and alkali as follows: cotton, nylon, acetate, bright viscose, dull viscose, and wool. While this order of reactivity of the fibers is somewhat less clear-cut in the case of sorption from soap solutions than from sodium hydroxide solutions, it appears on the whole to be generally applicable.

The ratio of fatty acid to alkali sorbed by the various fibers is shown in Fig. 2. It may be noted that in general this ratio decreases with increasing

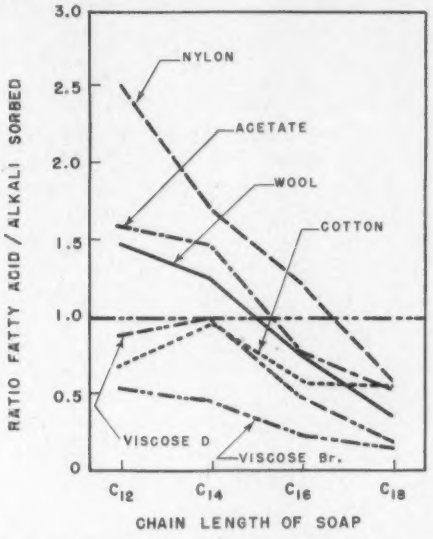

FIG. 2. *Effect of chain length of soap on ratio of fatty acid : alkali sorbed.*

chain length of the soaps. Cotton and viscose rayon show a preferential sorption of alkali with all of the soaps, whereas the other fibers show a preferential sorption of fatty acid with the lower molecular weight soaps but change over to preferential sorption of alkali with the higher soaps. While a preferential sorption of alkali has been reported in some cases (4, 6) there are no published data covering the sorption of fatty acid and alkali components of pure soaps over the range of fibers examined in the present work.

It is a well known fact, confirmed by the present data (Table II), that textile fibers sorb alkali from solutions. Since free alkali is present in all aqueous soap solutions owing to hydrolysis, it is reasonable to suppose that some sorption of this alkali by the fibers takes place. The degree of hydroly-

sis, and hence the concentration of free alkali in solution, increases with increasing chain length of the saturated soaps (15), and in the present case hydrolysis is no doubt accentuated owing to removal of the hydrolytic products by sorption. These are undoubtedly contributing factors in determining the ratio of fatty acid to alkali sorbed and may account in part for the decreasing ratio with increasing chain length of the soaps.

The addition of 0.01% of sodium hydroxide to the various soap solutions resulted in a decrease in the sorption of fatty acid by all the fibers (Table III). Nevertheless, in most cases some sorption of fatty acid was observed, and since, under these conditions, hydrolysis of the soap is believed to be completely suppressed (16), it may be concluded that this fatty acid was sorbed in the form of neutral soap molecules. The higher sorption observed in the absence of added alkali suggests that a considerable proportion of the total fatty acid sorbed may be attributed to the sorption of hydrolytic products, either free fatty acid or acid soap.

The effect of suppressed hydrolysis on fatty acid sorption is most pronounced in the case of sodium myristate solutions; whereas the maximum sorption of fatty acid from neutral soap solutions was obtained with the C_{14} soap, under conditions of suppressed hydrolysis the maxima are considerably reduced in magnitude and occur with the C_{16} soap. An exception to this general behavior occurs in the case of wool, and it is suggested that, owing to the high alkali sorption by this fiber, the concentration of free alkali in the soap solution was reduced to such an extent that hydrolysis of the soap was no longer completely suppressed.

It may thus be concluded that the sorption of soap by textile fibers is a complex process, the observed sorption being attributable to the more or less independent sorption of at least three components of the soap solution, viz.: neutral (unhydrolyzed) soap, free fatty acid and/or acid soap, and hydrolytic alkali. Whereas with carbon black, the removal of soap from solution is probably due entirely to physical adsorption, in the case of textile fibers the process is complicated by the fact that the fibers appear to show a strong affinity for certain components of the soap solution, which may be regarded as more nearly resembling chemical reaction than physical adsorption.

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References

1. ACHARYA, B. G. and WHEELER, T. S. Proc. Indian Acad. Sci., A,2 : 637-645. 1936.
2. ADAM, N. K. J. Soc. Dyers Colourists, 53 : 121-129. 1937.
3. AICKIN, R. G. J. Soc. Dyers Colourists, 60 : 60-65. 1944.
4. BRITISH RESEARCH ASSOCIATION FOR THE WOOLLEN AND WORSTED INDUSTRIES. J. Textile Inst. 13 : T127-T142. 1922.

5. CHAMPETIER, G. Anal. Chim. 20 (Ser. X) : 5-96. 1933.
6. COLT, E. W. and SNELL, C. V. Oil & Soap, 27 : 33-38. 1940.
7. EKWALL, P. Kolloid-Z. 101 : 135-149. 1942.
8. GARDINER, R. W. and SMITH, L. B. J. Am. Oil Chemists' Soc. 26 : 194-196. 1949.
9. HARRIS, J. C. Textile Research J. 18 : 669-678. 1948.
10. HOWLETT, F. and MARTIN, E. Shirley Inst. Mem. 18 : 235-240. 1941-43.
11. KLEVENS, H. B. J. Phys. & Colloid Chem. 52 : 130-148. 1948.
12. KOLTHOFF, I. M. and STRICKS, W. J. Phys. & Colloid Chem. 52 : 915-941. 1948.
13. LECOMPTE, G. C. and CREELY, J. W. Am. Dyestuff Reptr. 31 : 121-123. 1942.
14. LOTTERMOSER, A. Trans. Faraday Soc. 31 : 200-208. 1935.
15. MCBAIN, J. W., LAURENT, P., and JOHN, L. M. J. Am. Oil Chemists' Soc. 25 : 77-84. 1948.
16. MCBAIN, J. W. and MARTIN, H. E. J. Chem. Soc. 105 : 957-977. 1914.
17. MCBAIN, J. W. and SIERICHS, W. C. J. Am. Oil Chemists' Soc. 25 : 221-225. 1948.
18. NEVILLE, H. A. and HARRIS, M. Am. Dyestuff Reptr. 24 : 312-314. 1935.
19. NEVILLE, H. A. and JEANSON, C. A. J. Phys. Chem. 37 : 1001-1008. 1933.
20. NEVILLE, H. A., JEANSON, C. A., and SMITH, A. L. Am. Dyestuff Reptr. 22 : 565-566. 1933.
21. POWNEY, J. and JORDAN, D. O. Trans. Faraday Soc. 34 : 363-371. 1938.
22. PRESTON, C. Dyer, 101 : 144. 1949.
23. SHEDLOVSKY, L., MILES, G. D., and SCOTT, G. V. J. Phys. & Colloid Chem. 51 : 391-407. 1947.
24. SOOKNE, A. M. and HARRIS, M. J. Research, Natl. Bur. Standards, 25 : 47-60. 1940.
25. STAUFF, J. Z physik. Chem., A, 183 : 55-85. 1938.
26. WALKER, E. E. J. Chem. Soc. 119 : 1521-1537. 1921.
27. WEATHERBURN, A. S., ROSE, G. R. F., and BAYLEY, C. H. Can. J. Research, F, 27 : 179-193. 1949.
28. WOODMANSEY, A. J. Soc. Dyers Colourists, 35 : 169-171. 1919.

A SMALL FLUIDIZED SOLIDS PILOT PLANT FOR THE DIRECT DISTILLATION OF OIL FROM ALBERTA BITUMINOUS SANDS[1]

By W. S. Peterson and P. E. Gishler

Abstract

A new method of recovering oil from Alberta bituminous sand is described, in which the bituminous sand is fed directly into a hot fluidized sand bed. A clean dry distillation product is obtained amounting to 80% by volume of the bitumen in the feed. A description is given of the pilot plant.

Introduction

The increasing demand for oil in the western hemisphere has recently directed attention towards subsidiary sources. In the United States a great deal of research effort is being expended on methods of producing oil by hydrogenation of coal, the Fischer–Tropsch reaction, and the processing of oil shale.

In Canada no extensive oil shale deposits of commercial grade have been established. However, in northern Alberta is found one of the world's extensive oil occurrences known as the Alberta Bituminous sands. Estimates of its extent vary, but it is known to cover an area of over 1500 sq. miles. The bitumen content varies from a few per cent up to 17% by weight and the bed thickness from a few feet to over 200 ft. Several pools have been located with a bitumen content up to 80%. In one of the richest areas studied (5) a bitumen content of 200,000,000 barrels per square mile has been estimated. This is conveniently located in the Mildred – Ruth Lake area near the Athabaska River. A large part of the occurrence, however, is unsuited for development owing either to location, excessive overburden, or low oil content.

Separation

During the last 30 years a great deal of work has been done in an attempt to develop a process for the economic recovery of bitumen. Periodically this has been extended to small scale commercial operation. The work has been concentrated mainly on the use of water as a separating medium. There are many references in the literature describing this work, including those of Max Ball (1), K. A. Clark (2), and S. C. Ells (3). At present the Alberta Government is operating a demonstration separation plant at Bitumount using hot water and a diluent. The Bureau of Mines is operating a pilot plant in Ottawa, using cold water and a diluent.

Flash Distillation

The present paper deals with a dry method of recovering oil from bituminous sand, using the fluidized solids technique. Bituminous sand consists of

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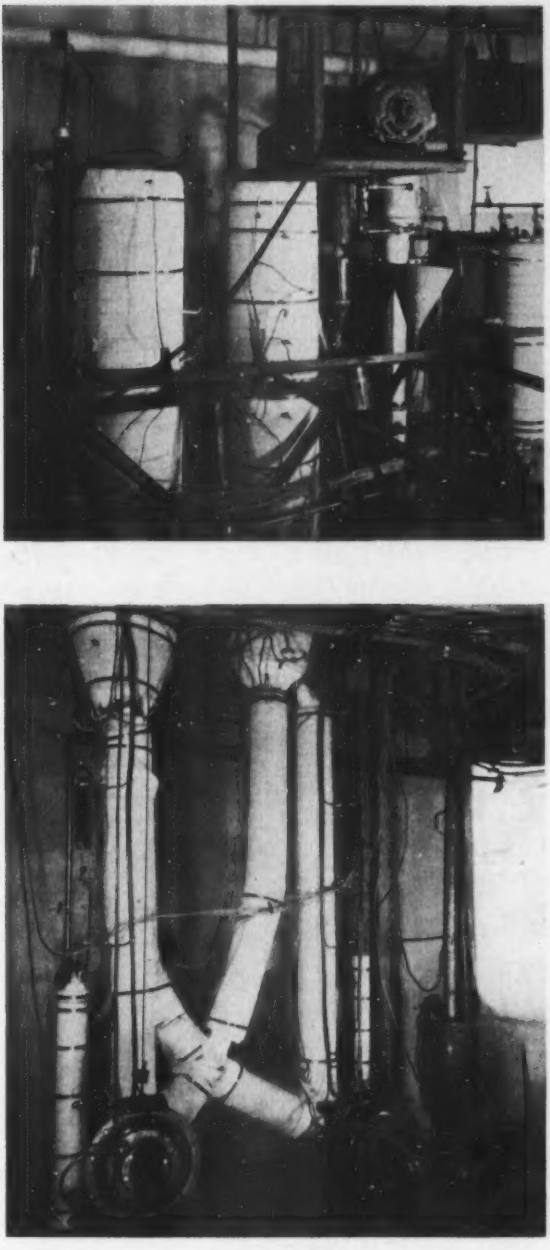

FIG. 1. *Pilot plant.*

individual fine sand grains each surrounded by a film of black viscous oil. It is more or less firmly compacted, the degree depending on sand grain size and viscosity of the oil.

The pilot plant design has been based on laboratory scale work which is described in the literature (4). In preliminary laboratory work it was found that when lumps of bituminous sand were dropped into a fluidized sand bed held at about 500° C., the oil flashed off immediately (a matter of several seconds) leaving free flowing individual grains of residual sand each coated with a thin, closely adhering film of coke. The oil produced had a much lower viscosity than the original bitumen.

Quantitative laboratory tests indicated an oil yield amounting to 76% of the bitumen content of the feed. The maximum oil yield and optimum operating temperature was at 500° C. It was found that below 460° C. distillation was sluggish, resulting in agglomeration of particles. Above 550° C. the oil yields fell off rapidly because of excessive cracking.

A laboratory study was also made of the combustion properties of the coke film adhering to the residual sand. Oxygen utilization remained quite high until the coke content of the residual sand was reduced below 0.2% in beds as shallow as 12 in. This indicated that no trouble should be encountered in using this as a fuel to supply the heat necessary for the process.

Pilot Plant Flow Sheet

A small pilot plant was therefore designed and built. It consisted essentially of two fluidized solids units, a still and a burner. Fig. 1 shows a picture of the plant and Fig. 2 the flow sheet. Bituminous sand is fed into the still.

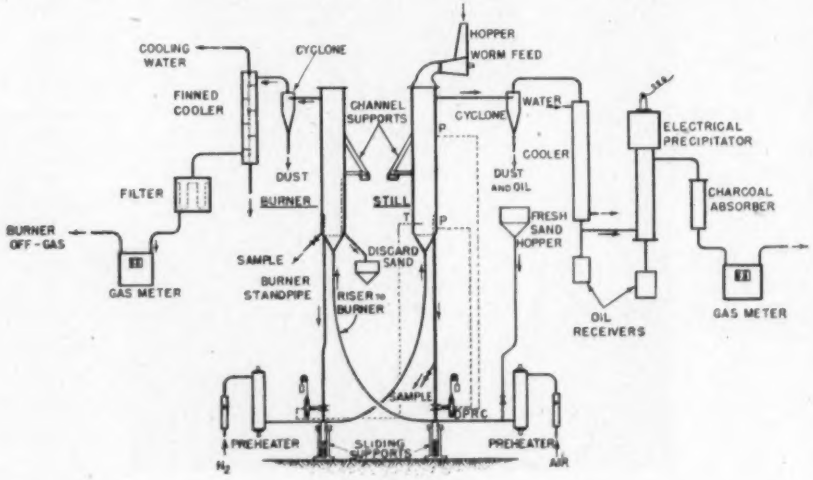

FIG. 2. *Pilot plant.*

The oil flashes off and is collected. The residual coked sand is withdrawn down a standpipe. It is picked up by a preheated air stream and blown into the burner. Combustion of the coke causes the sand to be heated up. Sufficient of this hot sand is recycled to the still to maintain it at the desired temperature. The oil on leaving the still begins to condense out as fine oil droplets suspended in the fluidizing gas which for the runs discussed here consisted of nitrogen. Dust, along with some of the oil, was removed by a cyclone designed for low pressure drop in order to avoid any leakage of gas through the feeder system. The off-gas was passed through a heat exchanger where more oil collected. An electrical precipitator removed the remainder of the heavy oil. The gas then passed through one of a set of three charcoal scrubbers. The hydrocarbons removed here consisted of gasoline and lighter fractions. This was recovered by steam distillation.

Equipment

The pilot unit has an over-all height of 15 ft. including the feeder, and is suspended through a well 2 by 8 ft. The rest of the equipment, with the exception of the gas meters and instruments, is in the immediate vicinity of this well so that the floor space occupied in the upper level is about 12 by 4 ft.

The still design is shown in Fig. 3. It is 6 in. in diameter and 6 ft. long and made of 14 gauge type 304 stainless steel. The maximum bed depth that can be used is about 3 ft. (0.6 cu. ft.). The still was designed to operate under adiabatic conditions as follows.

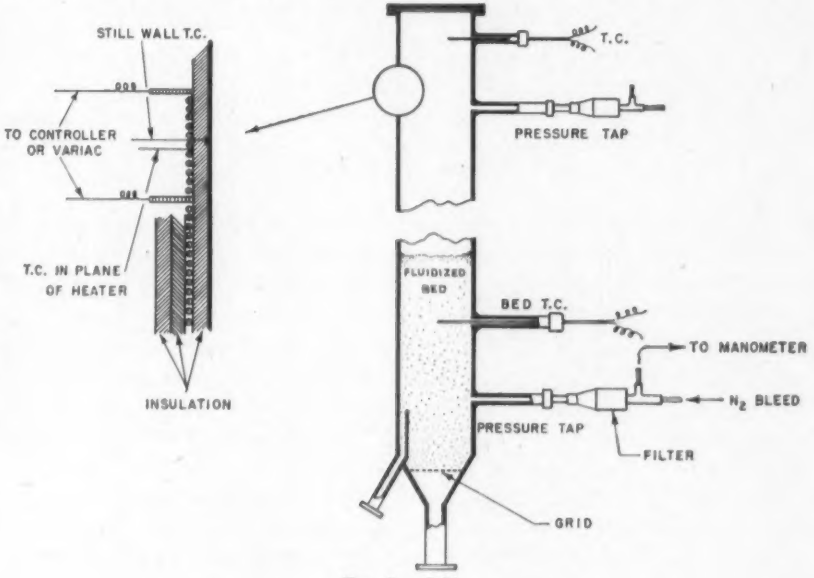

FIG. 3. *Still.*

The metal wall was covered by a layer of 1½ in. high temperature insulation and then wound with four heaters. These were covered by 3 in. of insulation and wrapped with woven asbestos tape. At the midsection of each heater one thermocouple registers wall temperature and a second the temperature of the winding. The input to the heaters was adjusted to keep these temperatures approximately equal.

The burner is similar in design to the still except that it is 9 in. in diameter and 6 ft. long. For rapid heating at the beginning of an experiment beaded resistance wire was wound directly onto the metal wall.

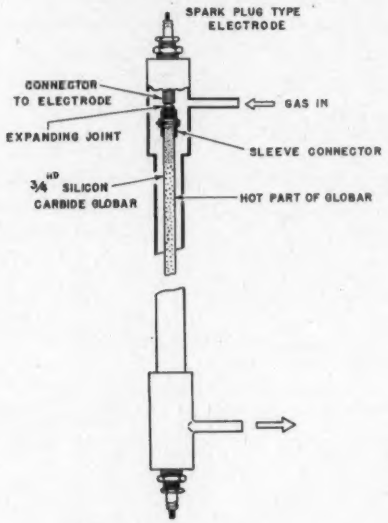

FIG. 4. *Gas preheater.*

The air and nitrogen were preheated by means of annular heaters consisting in each case of a silicon carbide element contained in a stainless steel tube. The details of the preheater are shown in Fig. 4. In order to obtain a high film coefficient the annulus was 1/8 in.

The collection system consisted of a cyclone for removal of dust, and a heat exchanger in which the heavy oil condensed to form a suspension of oil droplets in nitrogen. These were recovered by means of an electrostatic precipitator. The volatile hydrocarbons were removed by means of an activated charcoal scrubber.

The two important controls were those for maintaining the still bed at the required temperature and maintaining the desired bed depth. The source of heat was the hot recycled burnt sand. A temperature recorder-controller, actuated by a thermocouple in the still bed, controlled the operation of the

slide valve at the base of the burner standpipe, thus admitting the required amount of hot burnt sand into the still. The nitrogen carrying this sand was usually preheated.

The still bed depth was controlled by a bellows type differential pressure recorder-controller, which operated the slide valve at the base of the still standpipe.

There was found to be no particular need for automatic control equipment on the burner. The burner was run at a temperature about 200° C. above that of the still. The level of the burner bed was maintained by an overflow pipe passing through a trap to waste. The slide valves at the base of the still and burner standpipes were similar in design to those described by Trainer, Alexander, and Kunreuther (6), as were also the pressure tap filters.

Nitrogen and air were measured by means of rotameters. Two dry gas meters measured the burner and still off-gas volumes.

Auxiliary equipment, such as variacs, temperature recorders, and indicators, contained no unusual features. Glass manometers were used for measuring differential pressures. The system was adequately supplied with pressure taps and thermocouple wells.

Operation

The pilot plant was designed and operated to determine whether the process, as outlined above, could produce oil successfully from bituminous sand. Yields of oil, amount of deposited coke, and capacity of the unit are of primary interest.

The initial work, reported here, has included no long term tests, but has been confined to five-hour runs with feed rates of 60 to 120 lb. per hr. of bituminous sand. The pilot plant lined out rapidly and off-gas analyses, sand analyses, and yields changed but slightly after the first hour.

A summary of operational procedure follows.

Burnt sand was added to the burner and the power turned on full. When this sand had reached the operating temperature of the still, it was transferred to the still until the proper bed depth had been established. The depth in the burner was then adjusted by addition of more cold burnt sand. The temperature of the burner was allowed to rise to the operating temperature. Air was then replaced by nitrogen as the still bed fluidizing gas and the bituminous sand was fed at a steady rate.

Heavy oil was collected hourly from the cyclone, heat exchanger, and electrical precipitator and measured. The following were taken half-hourly: sand discard, burnt and coked sand samples, burner and still off-gas samples, manometer and thermocouple readings. Light oil was recovered from the charcoal absorbers at the end of each run by means of steam distillation.

Data

The feed used for most of the work to date was obtained from the deposit at Bitumount, Alberta. The composition varied slightly from drum to drum. This is shown in Table I.

TABLE I

COMPOSITION OF BITUMINOUS SAND

Bitumen, wt. %	13.4 – 14.7
Water, " %	0.4 – 0.3
Sand, " %	86.2 – 85.0

This material is somewhat coarser grained than that found farther south. A screen analysis of the sand residue is given in Table II.

TABLE II

SCREEN ANALYSIS OF SAND RESIDUE

On 35 mesh	12.6%
35 – 60 mesh	34.9
60 – 80 "	35.3
80 – 100 "	10.7
100 – 150 "	5.0
Through 150 mesh	1.2

The contained bitumen is of an asphaltic nature and was found to have the composition indicated in Table III.

TABLE III

COMPOSITION OF BITUMEN IN FEED, %

Asphaltous acids and anhydrides	0.9
Asphaltenes	20.1
Oily material	55.1
Resins	19.4
Ash	4.1
Sulphur	5.0

The significant data of two runs only will be presented at this time. In run No. B–4 a steady feed rate slightly higher than the designed capacity was used. In run No. B–6 the feed rate was varied up to double the designed capacity. The basis of design was 1 lb. per min. The data are shown in Table IV.

TABLE IV

OPERATING DATA

Run No.	*B-4*	*B-6*
Duration, hr.	5	5
Still bed depth, in.	36	36
Still bed temperature, ° C.	500	500
Burner bed depth, in.	36	36
Burner bed temperature, ° C.	700	700
Recycle ratio	—	4
Still retention time, min.	—	6
Feed rate, lb./hr.	67½	80-120
Total feed, lb.	337½	540
Oil recovery		
Heavy oil, Imp. gal.	3.66	6.1
Light oil, Imp. gal.	0.02*	0.2
Yield, vol. per cent	82	79
Still capacity, bbl./ft.³ day	0.8	1.2-1.6

**Charcoal not properly activated.*

The bulk of the product is a heavy oil. Of chief interest is the fact that this oil contains only traces of solids and water, and that, owing to the high temperature in the still, it has a viscosity much lower than that of the original bitumen. The analytical data are given in Table V.

TABLE V

HEAVY OIL ANALYSIS

Run No.	*B-4*	*B-6*
Color	Red brown	Red brown
Specific gravity, 60° F./60° F.	0.957	0.956
Viscosity, kin., centistokes		
100° F.	91.4	69.4
210° F.	8.39	7.26
Sulphur, %	4.0	4.0
Water, %	Trace	Trace
Solids, %	0.08	0.07
Distillation		
I.B.P., ° F.	415	404
5% recovered	—	436
10% "	500	492
20% "	568	560
30% "	588	588
40% "	618	644
50% "	632	676
60% "	636	—
65% "	—	684

Only about 3% of the total oil was recovered from the charcoal absorber as a light distillate. The properties of this oil are given in Table VI.

TABLE VI

LIGHT OIL ANALYSIS

Color	Yellow
Specific gravity, 60° F./60° F.	0.746
Distillation	
I.B.P., ° F.	128
5% recovered	156
10% "	170
20% "	188
30% "	206
40% "	225
50% "	244
60% "	268
70% "	300
80% "	324
90% "	360
95% "	380

Discussion

The maximum feed rate of 120 lb. per hr. (200 lb. per hr. per cu. ft. still bed) caused no difficulty in operation. However, at this feed rate, the coked sand passing down the still standpipe was slightly wetted with oil in spite of the nitrogen purge used. The use of a stripper should result in an increase in capacity.

Yields of oil were higher than the 76% obtained on a laboratory scale.

With the still bed at 500° C. and feed rates of the order mentioned, the coke deposit on the sand was not sufficient to maintain the required temperature differential between the burner and still. The use of a finer grained sand resulted in a higher coke content. However, if necessary, any thermal deficiency could be made up by using cracker gas or refinery residue, or by varying the conditions within the still.

This process is a new approach to the problem of recovering oil from bituminous sand. The chief advantage is believed to be that a distillation product free from water and solids is obtained directly from the sand in a single operation.

References

1. BALL, MAX W. Trans. Can. Inst. Mining Met. 44 : 58-91. 1941.
2. CLARK, K. A. and PASTERNACK, D. S. Ind. Eng. Chem. 24 : 1410-1416. 1932.
3. ELLS, S. C. Can. Dept. Mines. Mines Branch Report of Investigations, No. 632. 1926.
4. GISHLER, P. E. Can. J. Research, F, 27 : 104-111. 1949.
5. HUME, G. S. Trans. Can. Inst. Mining Met. 50 : 298-324. 1947.
6. TRAINER, R. P., ALEXANDER, N. W., and KUNREUTHER, F. Ind. Eng. Chem. 40 : 175-182. 1948.

VARIATIONS IN PROTEIN CONTENTS OF PLANTS, HEADS, SPIKELETS, AND INDIVIDUAL KERNELS, OF WHEAT[1]

I. LEVI[2] AND J. A. ANDERSON[3]

Abstract

Protein contents of individual kernels of wheat, representing random samples taken from two plots of 0.1 acre and two plots of 0.23 acre, were found to be distributed within samples in an approximately normal manner over a range of at least 6 percentage units with a standard deviation of 1.4 units.

Protein contents of grain of 68 Thatcher plants, comprising a 10 ft., 1-row plot, had a range of 2.7% and a standard deviation of 0.6%. Within plants, the average range for single heads was 1.7%; the maximum range was 4.9%. Heads with high protein contents tended to occur on the shorter tillers of plants containing more than three tillers.

Determinations were made on each of the kernels in three plants. Mean values for individual spikelets were normally distributed over a range of 5.1%; two extreme values, representing spikelets containing only one kernel, increased the range to 9.6%; the standard deviation for spikelets within heads was about 1.1%. Protein contents of spikelets tended to decrease towards the top from about the top third of the head; the top two spikelets of each head generally had decidedly lower protein contents than the remaining spikelets.

Within spikelets containing three kernels, the top kernel tended to be decidedly lower in protein content (mean, 14.7%) than the remaining two; the middle kernel (15.9%) tended to be slightly higher than the lowest one (15.7%). In spikelets containing only two kernels, the top one tended to be about 0.3% lower in protein content. Within plants, the protein contents of individual kernels were normally distributed over a range of about 6% with a standard deviation of 1.2%.

Canadian wheat is handled in bulk as a flowing commodity. During the movement from farms to seaboard, streams of wheat of the same grade, originating from widely scattered points, are gradually blended together in country elevators, railroad cars, terminal elevators, and lake boats. This process creates considerable uniformity in the quality of export shipments of each grade. Nevertheless, some variation continues to exist, particularly in protein content. Attempts to improve this situation depend primarily on knowledge of the sources of the variation. Exhaustive studies, some extending back to 1927, have been made of the protein contents of carlots and cargoes of Canadian wheat. The data have been summarized in Annual Reports of the laboratory and in a bulletin (2) published in 1943. The present paper traces variations in protein content to certain primary sources by dealing with data for individual kernels from single plants and from samples grown in rod-row and tenth-acre plots.

Methods

A single kernel of wheat, weighing about 0.03 gm., is too small for a macro determination of protein content. Grinding the kernel and taking an aliquot

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[2] *Chemist.*
[3] *Chief Chemist.*

part for a micro determination involves a considerable sampling error. The Hengar semimicro method (5) was therefore chosen a ssuitable for whole kernels. Considerable trouble was experienced in obtaining accurate and reproducible results. The technique finally adopted involved the use of micro burners with both gas and air control, of equipment with ground glass joints, of 0.002 to 0.003 gm. of selenium powder per test, and of $N/100$ standard reagents. A final test of the method was made with wheat ground to an impalpable powder in a ball mill. On the basis of 53 analyses of 0.03 gm. aliquots, the standard deviation of a single semimicro analysis was estimated to be 0.24 percentage unit. Corresponding statistics for the macro method range between 0.11 and 0.19 unit (1). The mean of the 53 semimicro analyses was 16.5%, and the same value was obtained for the mean of eight macro analyses.

Bulk samples were split with a Boerner sampler so as to segregate about twice as many subsamples as were required, each containing 7 to 13 kernels. Subsamples were then selected in random order and all kernels in each one selected were analyzed after drying overnight at 98° to 100° C. *in vacuo.*

Results for single kernels are reported without correction for moisture still remaining in the kernels, namely, about 3%. Results obtained by the macro method on ground wheat are reported on a dry basis. These differences in procedure cause semimicro results to average about 0.4% lower in apparent protein levels than macro results.

Samples from Small Plots

Analyses were made of random samples of individual kernels from four plots: Red Bobs and Marquis grown in 0.1 acre plots at Muddy Lake, Saskatchewan; and Marquis grown in 0.23 acre plots at Scott, Saskatchewan, and Fallis, Alberta. The last two plots comprised trials of 25 varieties each grown in randomized sextuplicate plots, of four rod rows each, from which the two inner rows were harvested. The samples thus represented six pair of rod rows arranged at random on a block measuring 81 by 126 ft. (0.23 acre).

Data for the protein contents of individual kernels are given in Table I. Each sample covers a protein range of at least 6%. While the number of kernels in each group is small, the data certainly suggest that the distribution among 0.5% protein ranges is approximately normal and symmetrical about the mean. It is interesting to note that the range covered by the 200 kernels of the last two samples, from 7% to 21%, is almost identical with the range for the protein contents of all carlots, over 200,000, of wheat analyzed in this laboratory during the past 20 years.

Individual Plants

Macro determinations of protein content of grain were made on 68 of 71 individual plants comprising a single 10 ft. row of Thatcher wheat. The

TABLE I

FREQUENCY DISTRIBUTION AMONG 0.5% PROTEIN RANGES OF SINGLE KERNELS FROM SMALL WHEAT PLOTS

Protein range, %	Red Bobs, Muddy Lake	Marquis, Muddy Lake	Marquis, Fallis	Marquis, Scott
7.0 - 7.5	—	—	2	—
7.5 - 8.0	—	—	2	—
8.0 - 8.5	—	—	5	—
8.5 - 9.0	—	—	6	—
9.0 - 9.5	—	—	8	—
9.5 - 10.0	—	—	6	—
10.0 - 10.5	—	—	8	—
10.5 - 11.0	3	—	10	—
11.0 - 11.5	5	—	15	—
11.5 - 12.0	8	1	11	—
12.0 - 12.5	13	4	9	—
12.5 - 13.0	22	7	7	—
13.0 - 13.5	39	15	8	—
13.5 - 14.0	24	18	1	—
14.0 - 14.5	44	12	2	2
14.5 - 15.0	18	11	—	2
15.0 - 15.5	13	17	—	2
15.5 - 16.0	9	8	—	2
16.0 - 16.5	7	2	—	8
16.5 - 17.0	2	4	—	9
17.0 - 17.5	4	3	—	17
17.5 - 18.0	1	—	—	16
18.0 - 18.5	—	—	—	13
18.5 - 19.0	—	—	—	8
19.0 - 19.5	—	—	—	7
19.5 - 20.0	—	—	—	6
20.0 - 20.5	—	—	—	3
20.5 - 21.0	—	—	—	3
21.0 - 21.5	—	—	—	2
Total	212	102	100	100
Standard deviation	1.3	1.2	1.6	1.5

mean protein content and the standard deviation were 16.7% and 0.6%. Minimum and maximum values were 15.3% and 18.0%, so that the range was 2.7%. The frequency distribution among 0.5% protein ranges, given below, suggests no abnormalities.

Protein range, %	Number of plants
15.0 – 15.5	1
15.5 – 16.0	8
16.0 – 16.5	21
16.5 – 17.0	18
17.0 – 17.5	15
17.5 – 18.0	5

Numbers of kernels per plant ranged from 44 to 412 with a mean of 99, and corresponding figures for weight of grain per plant were 0.76 gm. to 10.67 gm., with a mean of 2.65 gm. No significant correlation was found between

protein content and either number or weight of kernels. There were, of course, high correlations between the total protein in the grain of each plant and both the number and weight of kernels.

Individual Heads

Macro determinations of protein content of grain were made for each of the individual heads from 24 of the plants. The data are shown in Table II in which the plants are arranged in increasing order of protein content.

TABLE II

PROTEIN CONTENT OF INDIVIDUAL HEADS

Plant mean	Head number							Range, %
	1	2	3	4	5	6	7	
15.5	15.6	15.4	15.4	15.9	—	—	—	0.5
15.8	15.5	16.3	15.1	16.4	—	—	—	1.3
15.9	15.7	15.3	16.4	15.7	16.3	16.0	16.2	1.1
16.1	15.6	16.2	16.6	16.0	—	—	—	1.0
16.2	15.6	15.7	17.0	16.8	—	—	—	1.4
16.4	16.1	16.5	16.0	20.1	—	—	—	4.1
16.4	16.5	16.9	16.3	15.6	—	—	—	1.3
16.4	16.2	17.2	16.3	16.7	19.2	—	—	3.0
16.4	16.4	16.7	16.2	—	—	—	—	0.5
16.5	16.0	16.6	15.7	17.0	20.0	—	—	4.3
16.5	16.9	16.1	16.3	—	—	—	—	0.8
16.6	16.3	16.7	16.8	16.4	—	—	—	0.5
16.6	16.5	16.2	17.7	—	—	—	—	1.5
16.6	16.7	16.9	16.2	16.4	16.3	17.0	—	0.8
17.0	16.9	17.0	17.2	—	—	—	—	0.3
17.0	16.9	16.8	18.8	—	—	—	—	2.0
17.1	21.3	16.5	16.7	16.4	17.8	—	—	4.9
17.2	17.2	16.3	17.9	19.0	—	—	—	2.7
17.2	16.8	17.2	17.0	19.5	—	—	—	2.7
17.3	17.7	17.4	17.1	16.8	—	—	—	0.9
17.4	16.9	17.9	18.0	—	—	—	—	1.2
17.4	17.4	17.4	—	—	—	—	—	0.0
17.4	16.9	17.8	17.0	17.4	18.6	17.4	—	1.7
17.6	17.3	17.0	17.6	18.0	18.7	—	—	1.7
Means:								
3-Head	16.7	16.6	16.8	—	—	—	—	
4-Head	16.6	16.6	16.5	17.1	—	—	—	
5-Head	17.2	16.8	16.6	16.8	18.1	—	—	

Heads are numbered in order of decreasing length of the tillers, i.e., Head No. 1 was borne by the longest tiller (See Fig. 1,A).

The first of the means given at the bottom of the table is for Heads 1, 2, and 3 of the 23 plants having three or more heads. There is no evidence that constant differences in protein content exist between Heads 1, 2, and 3. Whether the longest tiller was produced first, or whether the head on it flowered first, is not known; accordingly, no inferences can be drawn from this failure to establish average differences between the heads on the three longest tillers.

The means for the 17 plants having four or more heads, and for the seven plants having five or more, suggest that the heads on the shorter tillers tend to be higher in protein content. Detailed examination of the data indicate that this is often but not invariably true.

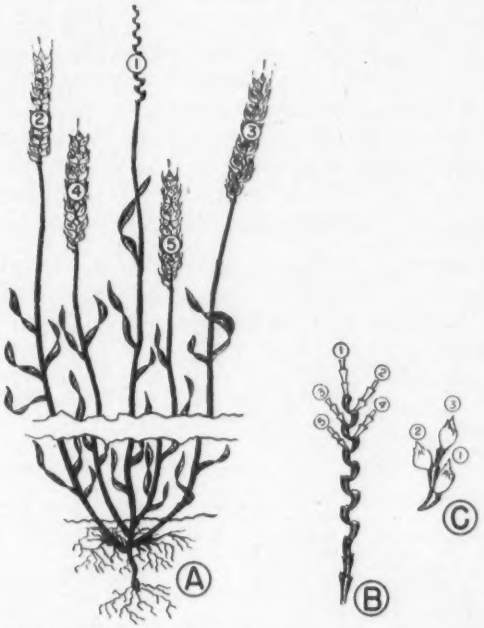

FIG. 1. *Diagram showing systems for numbering tillers (A), spikelets (B), and florets (C).*

Ranges for protein contents of heads within plants varied from 0% to 4.9% with a mean of 1.7%. Protein contents of all 99 heads on the 24 plants covered a range of 6.2%, from 15.1% to 21.3%, with a mean of 16.7% and a standard deviation of 1.1%. The frequency distribution among 0.5% protein ranges follows:

Protein range, %	Number of heads
15.0 – 15.5	4
15.5 – 16.0	10
16.0 – 16.5	26
16.5 – 17.0	23
17.0 – 17.5	18
17.5 – 18.0	7
18.0 – 18.5	2
18.5 – 19.0	3

Protein range, %	Number of heads
19.0 – 19.5	2
19.5 – 20.0	1
20.0 – 20.5	2
20.5 – 21.0	0
21.0 – 21.5	1

The major part of the distribution, from 15% to about 18 or 18.5%, appears to be approximately normal and symmetrical. But taken as a whole, the distribution is asymmetrical, since 11 of the heads have very high protein contents of 18.0% or more. With one exception, these high-protein heads occurred on the third, fourth, or fifth longest tiller.

Individual Spikelets

Semimicro determinations were made of the protein contents of each kernel in each of three plants. Spikelets contained from one to three kernels, and the positions of these in the spikelets and positions of the spikelets on the heads were recorded.

TABLE III

PROTEIN CONTENTS OF INDIVIDUAL SPIKELETS

Spikelet number	Plant 1				Plant 2				Plant 3				Mean
	Head 1	Head 2	Head 3	Mean	Head 1	Head 2	Head 3	Mean	Head 1	Head 2	Head 3	Mean	
1	15.0	11.5	12.4	13.0	13.2	12.4	12.6	12.7	13.1	13.9	13.9	13.6	13.1
2	–	13.7	13.4	13.6	15.5	12.6	–	14.0	15.8	15.4	13.7	15.0	14.3
3	17.1	12.8	15.2	15.0	15.6	13.9	13.5	14.3	15.4	15.6	14.5	15.2	14.8
4	16.6	14.9	14.5	15.3	14.0	15.3	12.5	13.9	15.4	15.6	14.8	15.3	14.8
5	17.5	14.9	14.3	15.6	15.0	14.9	13.8	14.6	15.4	15.4	15.7	15.5	15.2
6	16.2	15.5	15.6	15.8	15.0	14.7	13.8	14.5	15.7	15.3	16.0	15.7	15.3
7	14.8	15.2	16.1	15.4	15.1	14.5	15.0	14.9	15.7	15.8	15.5	15.7	15.3
8	15.8	16.3	15.7	15.9	14.2	15.4	16.3	15.3	16.2	15.8	16.1	16.0	15.7
9	14.9	15.0	15.4	15.1	15.5	16.1	14.8	15.5	15.6	16.1	15.4	15.7	15.4
10	15.3	17.4	16.2	16.3	15.1	16.2	14.3	15.2	15.9	16.1	16.8	16.3	15.9
11	16.3	15.5	15.0	15.6	15.9	15.2	14.4	15.2	16.4	16.7	15.8	16.3	15.7
12	15.1	16.0	16.1	15.4	14.8	15.1	14.3	14.7	15.1	15.5	15.6	15.4	15.2
13	–	14.7	15.8	15.2	15.2	15.6	14.1	15.0	–	15.4	15.7	15.6	15.2
14	–	17.1	15.1	16.1	15.2	15.4	14.6	15.1	–	21.1	16.0	18.6	16.4
15	–	–	–	–	16.9	15.2	14.0	15.4	–	–	17.1	17.1	15.8
16	–	–	–	–	–	–	14.6	14.6	–	–	–	–	14.6
Range	2.7	5.9	3.8		3.7	3.8	3.8		3.3	7.2	3.4		

Table III shows the average protein content of each spikelet in each head of each of the three plants. Spikelets are numbered consecutively from the top to the bottom of the head (Fig. 1,B), so that data for the top spikelet appear at the top of the table. In seven of the nine heads, the top or the top two spikelets have decidedly lower protein contents than the remaining

spikelets. In the other two heads, the top spikelet is also low in protein content, but a slightly lower value is given by another spikelet. Means for all heads, given on the extreme right, suggest that protein content tends to decrease from about the eighth to the top spikelet. This trend is also apparent in the means for each of the three plants, but is partially obscured by various irregularities in data for individual heads, particularly in Head 1 of Plant 1. Data in the last line of the table suggest that a range of about 3.5 percentage units occurs within the average head between the spikelets of highest and lowest protein content. Two heads showed much wider ranges, but these are due to a spikelet of very high protein content on one head and a spikelet of very low protein content on the other. Taken as a group, the spikelets for the three plants exhibit an extraordinarily wide protein range, 9.6%. However, a large part of this is contributed by the two extreme values (11.5 and 21.1), and if these are disregarded the range is reduced to 5.1%.

TABLE IV

FREQUENCY DISTRIBUTION AMONG 0.5% PROTEIN RANGES OF SPIKELETS FROM SINGLE PLANTS

Protein range, %	Plant 1	Plant 2	Plant 3	All plants
11.5 - 12.0	1	—	—	1
12.0 - 12.5	1	1	—	2
12.5 - 13.0	1	3	—	4
13.0 - 13.5	1	1	1	3
13.5 - 14.0	1	4	3	8
14.0 - 14.5	1	7	—	8
14.5 - 15.0	6	7	2	15
15.0 - 15.5	10	13	8	31
15.5 - 16.0	6	5	16	27
16.0 - 16.5	6	3	7	16
16.5 - 17.0	1	1	2	4
17.0 - 17.5	3	—	1	4
17.5 - 18.0	1	—	—	1
21.0 - 21.5	—	—	1	1
Standard deviation	1.3	1.0	1.2	1.2

Frequency distributions for spikelets among 0.5% protein ranges, for each plant and for all plants, are given in Table IV. The data show that the protein contents for most spikelets in each plant tend to fall close to the mean for the plant. But a few extreme values occur within each plant. The distribution for all plants appears to be approximately normal and symmetrical.

Individual Kernels

Five spikelets of Plant 1, nine of Plant 2, and eight of Plant 3, had three florets containing kernels. In each spikelet, the lowest floret (and its kernel) on the rachilla was numbered "one", the second lowest "two", and the top floret "three". The top floret, No. 3, is the one in the center when the spikelet is viewed from the side (Fig. 1,C).

Table V shows the protein contents for each of the three kernels in each spikelet. In 19 of the 22 spikelets, Kernel No. 3 had the lowest protein content; and in 13 of the 22, Kernel No. 2 had the highest protein content. Mean values over all spikelets were: Kernel 1, 15.7%; Kernel 2, 15.9%; and Kernel 3, 14.7%. There is apparently a slight tendency for Kernel No. 2 to be a little higher in protein content than Kernel No. 1, and a definite tendency for Kernel No. 3 to be decidedly lower in protein content than the others.

TABLE V

PROTEIN CONTENTS OF INDIVIDUAL KERNELS IN SPIKELETS CONTAINING THREE KERNELS

Plant 1			Plant 2			Plant 3		
Kernel 1	Kernel 2	Kernel 3	Kernel 1	Kernel 2	Kernel 3	Kernel 1	Kernel 2	Kernel 3
15.0	15.8	14.9	14.6	15.3	16.0	16.0	16.1	15.6
15.9	16.5	14.9	16.0	17.0	14.2	15.6	17.2	15.1
15.9	14.0	14.8	15.2	16.7	14.1	15.8	17.4	12.6
16.4	13.9	14.1	16.0	15.2	14.2	16.3	16.8	14.9
16.2	17.1	15.0	16.2	16.2	15.3	16.1	15.8	15.5
—	—	—	15.7	14.5	13.9	15.6	15.7	15.3
—	—	—	14.1	15.3	13.0	15.8	16.0	15.3
—	—	—	15.4	15.0	14.9	16.5	15.7	15.0
—	—	—	14.9	16.4	14.5	—	—	—

Two florets contained kernels in 24 spikelets of Plant 1, 22 of Plant 2, and 26 of Plant 3. Mean protein contents for Kernels No. 1 and No. 2 in the three plants follow:

Plant	Kernel No. 1	Kernel No. 2
1	15.7	15.3
2	15.1	14.7
3	15.8	15.6

The data suggest that when there are only two kernels in a spikelet the top one tends to have the lower protein content. This situation occurred in 12 of 24 spikelets in Plant 1, 15 of 22 in Plant 2, and 16 of 26 in Plant 3. Accordingly, it appears that a generalization is barely warranted.

Frequency distributions for kernels among 0.5% protein ranges, for each plant and for all plants, are given in Table VI. Protein contents of kernels within each plant cover a range of about 6 percentage units, with one or two values well beyond this range. Distributions within plants are fairly normal. The over-all range for kernels of all three plants is identical with the range for spikelets, since spikelets giving extreme values contained only one kernel.

TABLE VI

FREQUENCY DISTRIBUTION AMONG 0.5% PROTEIN RANGES OF SINGLE KERNELS FROM SINGLE PLANTS

Protein range, %	Plant 1	Plant 2	Plant 3	All plants
11.0 - 11.5	1	—	—	1
12.0 - 12.5	1	1	—	2
12.5 - 13.0	1	5	1	7
13.0 - 13.5	1	2	1	4
13.5 - 14.0	4	8	3	15
14.0 - 14.5	4	14	3	21
14.5 - 15.0	16	18	9	43
15.0 - 15.5	16	17	15	48
15.5 - 16.0	9	10	21	40
16.0 - 16.5	12	6	19	37
16.5 - 17.0	2	2	5	9
17.0 - 17.5	4	2	4	10
17.5 - 18.0	3	1	1	5
19.5 - 20.0	1	—	—	1
21.0 - 21.5	—	—	1	1
Total	75	86	83	244
Standard deviation	1.3	1.1	1.1	1.2

Relation Between Protein Content and Kernel Weight

As a by-product of the investigation, some information was obtained on the relations between protein content and kernel weight. Pooled results, for all nine heads, yielded a low but significant positive correlation ($r = .15^{*}$) between protein contents and weights of individual kernels within heads. Further examination suggests that this is due largely to a much higher correlation within spikelets. Analysis of data for the three-kernel spikelets yielded a highly significant positive correlation ($r = .59^{**}$); i.e., a kernel having a weight above the average weight for the spikelet tends to have a higher protein content than the average for the spikelet. No significant correlation was found for mean protein contents and kernel weights of spikelets.

Discussion

Though the data presented in this paper are not extensive, they amplify prior information and thus provide for more complete visualization of sources of variation in the protein content of Canadian wheat. Four sources of variation can be usefully distinguished. Firstly, there is the variation that exists among the protein contents of individual kernels within each plant. Secondly, there is the variation that occurs among the mean protein contents of closely adjacent plants of a single variety grown in essentially the same environment. Thirdly, there is the variation that occurs in mean protein contents of lots of the same variety grown under widely different environmental conditions. And fourthly, there is the variation that occurs among the mean protein

contents of lots of different varieties grown under essentially identical conditions. The present study deals primarily with the first two of these sources, and with the third, but to a lesser extent that hardly merits discussion.

A paper dealing with the variations in protein content among individual kernels of single wheat plants was published in 1936 by Knyaginichev and was followed by a second paper dealing with other cereals. Unfortunately, only English summaries of these Russian papers (6, 7) are available to the present authors, and these do not contain any ranges or distributions of protein contents.

Knyaginichev studied thirteen wheat varieties and divided these into two classes: those that yielded kernels of relatively uniform quality and for which no correlation existed between protein content and weight of kernel; and those characterized by a wide range of protein contents among kernels and a high correlation between protein content and weight. He found that the middle spikelets of an ear produced kernels of a higher average protein content than the upper and lower spikelets, and that, within the limits of single spikelets, the larger kernels had higher protein contents. The last of these generalizations applies to three-kernel spikelets of Thatcher wheat, as does the statement that upper spikelets are lower in protein content than middle spikelets. On the other hand, the present study provides no evidence that the lower spikelets are also lower in protein content than middle spikelets. It may be added, as a point of interest, that Knyaginichev attributes differences in protein content between kernels within a spikelet chiefly to differences in the dates of opening of the florets.

Since a range of at least 6% in protein content, and probably more, can be expected for the individual kernels of a single head, this source of variation is obviously of major significance. Within a single plant, there must also be added the variation that so frequently exists among the average protein contents of the different heads. On the average, the range involved is of the order of 1.7%, but may be much wider. As Knyaginichev has noted, this range is narrower than that for individual kernels.

An explanation of the difference in mean protein content between heads has been offered by Gericke (4). He planted wheat in soil deficient in nitrogen supply in order to restrict the early tiller formation, and subsequently supplied nitrogen, 90 days after planting, to obtain new tiller formation. This procedure provided an ample supply of nitrogen during the later growth period of some tillers and in an earlier period to others. The former produced grain of much higher protein content. He also found the interval between the times of ripening of two heads was directly related to the difference in protein content between them. The situation is obviously complicated. Protein content is a ratio of protein to nonprotein (mainly starch) constituents of the grain. A basic explanation of differences in protein content must thus relate to the rate and duration of translocation of both the protein and nonprotein constituents to the developing and maturing grain. Moreover,

respiration of the grain must also be involved, since this reduces the amounts of carbohydrates in the kernel and thus increases the ratio of protein to non-protein constituents.

A range of 2.7% in mean protein content of plants within a 10 ft. row seems relatively enormous. In addition to differences in the potential ability of various kernels to produce identical plants, differences in the structure and composition of the soil surrounding the germinating seeds probably affect early development. Some seed probably gain an early advantage from a favorable micro-environment and exploit this at the expense of their neighbors. The chances of two adjacent seeds having equal opportunities for development at all times must be relatively small. Wide differences among the plants grown on any considerable area, and resulting differences in the protein content of the grain they produce, must thus be expected. Since the present study was designed to establish what variations exist in protein content, rather than to elucidate the causes of the variation, further speculation about causes is hardly warranted.

For practical purposes, this paper presents quantitative data that offer direct support for inferences about variations in protein content that could be drawn from less detailed studies. For example, Malloch and Newton (8) found a maximum spread of 3.5% in protein content among 50 samples obtained from cutting 18 ft. rows from locations scattered over a field of about 3 acres that was reasonably level and did not show any obvious variations in soil. Various studies, reviewed by Bailey (3), have been made of the protein contents of "starchy" and "vitreous" kernels selected from the same sample. Differences of 2% to 3% in protein content have been found, but the size of the fields from which the samples were taken is rarely stated. From investigations such as these, it could be inferred that relatively large differences in the protein contents of individual kernels existed within samples. Additional information on the extent of these variations has now been provided.

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References

1. American Association of Cereal Chemists. Cereal laboratory methods. 5th ed. Am. Assoc. Cereal Chem. St. Paul. 1947.
2. Anderson, J. A. and Eva, W. J. Variations in the protein content of Western Canadian wheat. Board of Grain Commissioners Grain Research Lab. Bull. 4. Winnipeg. 1943.
3. Bailey, C. H. Minn. Agr. Exptl. Sta. Tech. Bull. 147. 1941.
4. Gericke, W. F. Science, 71 : 73-74. 1930.
5. Henwood, A. and Garey, M. R. J. Franklin Inst. 221 : 531-538. 1936.
6. Knyaginichev, M. I. Bull. Applied Botany, Genetics, Plant Breeding. U.S.S.R. Ser. III. 15 : 28-30. 1936.
7. Knyaginichev, M. I. Bull. Applied Botany, Genetics, Plant Breeding. U.S.S.R. Ser. III. 15 : 64-65. 1936.
8. Malloch, J. G. and Newton, R. Can. J. Research, 10 : 774-779. 1934.